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Description

The present invention refers to new supported components of catalysts for the polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is an alkyl with 1—4 carbon atoms or an aryl, and of mixtures of such olefins 5 with each other and/or with ethylene, and to the catalysts obtained from such components.

In earlier patent applications in the name of the Applicant there have been disclosed catalysts endowed with high activity and high stereospecificity, obtained from metallorganic Al compounds, silicon compounds containing Si—O—C, Si—OCOR or Si—NR₂ bonds and from a solid comprising a halogenated titanium compound and an electron-donor compound, both supported on an active Mg halide, the 10 electron-donor compound being chosen among specific classes of esters.

JP—A—79 94,590 (C.A. 92,7198d) relates to a solid catalyst compound prepared from an electron donor-treated Mg-halide and a Ti halide optionally treated with an electron donor.

JP—A—116,777 (Jap. Pat. Gaz., 15—21 April 1981, page 7) is concerned with catalysts for the polymerization of alphaolefins, comprising Ti components supported onto Mg-halide, conventional 15 electron-donor compounds in the form of esters, ethers, amines and the like, organo-Al compounds and silicon compounds (silanes).

It has now been unexpectedly found that it is possible to prepare highly active and highly stereospecific catalysts also by employing electron-donor compounds different from those described in the earlier patent applications, provided that the employed electron-donor compound belongs to certain 20 classes of compound, as specified hereinafter, and is for at least 70% by mols extractable from the solid catalyst component by reaction under standard conditions with Al-triethyl, and that the surface area of the product after extraction is not less than 20 m²/g.

The catalysts of the invention comprise the product of the reaction between at least the following components:

- 25 a) an Al-alkyl compound, preferably an Al-trialkyl or a compound containing two or more Al atoms linked to each other through oxygen or nitrogen atoms or through SO₄ or SO₃ groups;
- b) an electron-donor-compound (or Lewis base) which, under the standard conditions of measurement as indicated hereinafter, is reactive towards MgCl₂ but which results not to be completely complexed with AlEt₃ at the equivalent point of a potentiometric titration under standard conditions;
- 30 c) a solid comprising a Ti halide and an electron-donor compound both supported on a Mg halide, such electron-donor compound being selected from the classes of: ethers, ketones, lactones, electron-donor compounds containing N, P and/or S atoms, and from the following esters:
 - 1) hydrocarbyl esters of linear saturated dicarboxylic acids containing from 2 to 5 C atoms;
 - 2) esters of unsaturated polycarboxylic acids, in which two carboxyl groups are linked to vicinal, double bond-forming carbon atoms and in which the hydrocarbyl radical or radicals of the COOR groups are linear saturated or unsaturated radicals or cycloaliphatic radicals with 1—20 C atoms or hydrocarbyl esters of unsaturated linear or branched polycarboxylic acids with 1—20 carbon atoms, in which the carboxy groups are not linked to vicinal double bond-forming carbon atoms;
 - 3) hydrocarbyl esters of aromatic meta- and para-dicarboxylic acids and hydrocarbyl esters of aromatic polycarboxylic acids containing more than two carboxyl groups;
 - 4) hydrocarbyl esters of aromatic hydroxy compounds containing the OH groups in meta- or para-position, and esters of aromatic hydroxy acids the OH groups of which are in meta- or para-position with respect to the carboxyl group;
 - 5) esters RCOOR' the hydrocarbyl groups R and R' of which, which can be the same or different, are linear saturated or unsaturated radicals or cycloaliphatic radicals having from 1 to 20 carbon atoms, or R is an aryl, alkylaryl or cycloalkyl with 5—20 carbon atoms and R' is a hydrocarbyl radical or a heterocyclic ring with 5—7 atoms in the ring;
 - 6) hydrocarbyl esters of polycarboxylic acids in which at least one carboxyl group is linked to an aromatic ring and at least one other is linked to a carbon atom of an aliphatic group or to a cycloaliphatic ring or at least two carboxyl groups are linked to an aromatic ring through an alkylene group;
 - 7) esters of aromatic polycarboxylic acids containing at least two non-condensed aromatic rings, each of which bear a carboxyl group;
 - 8) esters of carbonic acid with glycols and carbonic acid derivatives of formula RO—CO—OR' wherein R and R' are the same or different acyl groups with 1—20 carbon atoms;
 - 9) esters of polyols and of monohydroxy-phenols;
 - 10) hydrocarbyl esters of acetylenic acids; the electron-donor compound being extractable from the solid for at least 70% by mols with Al-triethyl under standard measurement conditions, and the surface area of the solid subjected to extraction being higher than 20 m²/g.
- 60 Electron-donor compounds belonging to the above specified classes and suitable for the preparation of the catalyst components of the invention are: diisoamyl ether, diisobutyl ether, benzophenone, triphenyl phosphite, phenyl propionate, di-n-butyl succinate, diisobutyl succinate, di-n-butyl malonate, diethyl allylmalonate, di-n-butyl maleate, ethyl and propyl trichloroacetate, POCl₃, triphenylphosphine, α - methyl - α - phenyl - butyrolactone, 1,6-hexandiol di - p - toluate, 1,4-butandiol di - p - toluate, ethyl benzoyl carbonate

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(C₆H₅CO—O—CO—OC₂H₅),

diisobutyl ester of o-phenylene diacetic acid. It is understood that the above classes of esters include also the derivatives thereof as for instance the derivatives containing halogen atoms or unsaturated hydrocarbyl radicals. Ethyl trichloroacetate and diethyl allyl malonate listed above are examples of such derivatives.

All the above compounds are extractable from the solid catalyst component for at least 70% by mols by reaction with Al-triethyl. The surface area of the solid after the treatment with Al-triethyl is higher than 20 m²/g and in the case of very active catalysts higher than 100 m²/g and in general comprised between 100 and 300 m²/g.

In the case of weak electron-donors, as certain ethers, it has been found that the ether can be substantially removed from the catalytic solid during the preparation if the latter comprises treatments with excess TiCl₄ and/or washings with halogenated solvents. Nevertheless, also these catalyst components fall within the scope of the present invention. It is understood that the above donor compounds, when subjected to the extractability test with Al-triethyl before the above mentioned treatments, comply with the test.

It has been found that it is possible to obtain catalyst components according to the invention also by employing certain electron-donor compounds, such as alkyl, cycloalkyl or aryl esters of aromatic monocarboxylic acids, which in the preparation conditions hitherto known do not form catalyst components satisfying the requirements of this invention. The components according to the invention and containing the above esters are prepared by methods which consist in hot washing with a halogenated hydrocarbon solvent a co-ground mixture comprising the ester, the Ti compound and the Mg halide.

For Ti halides and electron-donor compounds supported on a Mg dihalide are meant the compounds not extractable from component c) after treatment with boiling 1,2-dichloroethane for 2 hours (concentration of the solid in the suspension: 5% by weight).

The compounds reactive towards MgCl₂ are those which under the standard conditions of the reaction remain fixed on the Mg halide for at least 20% by mols.

Components a), b) and c) are reacted with each other in whichever order; nevertheless, components a) and b) are preferably pre-mixed before being contacted with component c).

Component c) can be pre-mixed with component a) and/or with component b). The pre-mixing of a) and b) is carried out at temperatures usually comprised between room temperature and the temperature employed in the polymerization.

The pre-reaction of c) and b) can be carried out also at higher temperatures. Compound b) can also be incorporated in and reacted with component c) itself.

Component b) is reacted in a molar ratio with respect to the halogenated Ti compound supported on component c) of at least 1, and in a molar ratio with respect to the Al-alkyl compound employed as component a) lower than 20 and preferably comprised between 0.05 and 1. Ratios higher than 1 can be employed with compounds b) not complexing or only weakly complexing Al-triethyl also under conditions promoting such complex formation.

In component c) the molar ratio between the Mg dihalide and the halogenated Ti compound supported on it is comprised between 1 and 500, and the molar ratio between the halogenated Ti compound and the electron-donor both supported on the Mg dihalide is comprised between 0.1 and 50.

The electron-donor compound as defined in b) does not show at the equivalent point of the titration test with Al-triethyl (carried out under the standard conditions indicated hereinafter) any logarithmic variation of potential, i.e. a wave, in the titration curve.

A completely different situation occurs in the case of amines like isoquinoline or esters like ethyl-p-toluate or ethylbenzoate, wherein the titration curve shows a wave at the equivalent point. The absence of a wave at the equivalent point indicates that electron-donor compound b) is present, at least in part, in not complexed form with Al-triethyl.

Electron-donor compounds containing active hydrogen atoms reactive towards Al-triethyl, i.e. capable of substitution reactions with Al-triethyl, are prereacted with Al-triethyl, before subjecting the same to the complexation test. In the titration test the equivalent point is generally referred to the use of 1 mol of Al-triethyl per mol of donor.

Compounds b) can be used in mixture, in a wide range, with donors forming complexes with Al-triethyl when titrated according to the test set forth above.

The titration of the mixtures containing significant amounts of the complexing donors, shows the potential variation due to the presence of said complexing donors.

However the polymerization performance of the catalysts obtained by using the above mixtures as component b) is not significantly reduced by the presence of the complexing donor.

The compound b) is selected in particular from compounds of general formula:

R_mSiY_nX_p

wherein:
R is an alkyl, alkenyl, aryl, arylalkyl or cycloalkyl radical with 1—20 carbon atoms;

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Y is an —OR', —OCOR' or —NR'₂ radical in which R', the same as or different from R, has the same meaning as R;

X is a halogen or hydrogen atom or a —OCOR'' or —NR''₂ group in which R'', the same as or different from R', has the same meaning as R'; m, n, p are numbers comprised:

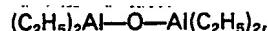
5 m from 0 to 3, n from 1 to 4 and p from 0 to 1; m+n+p is equal to 4.

Preferred silicon compounds are: phenyl alkoxy silanes, as phenyl triethoxy or phenyl trimethoxy silane, diphenyl dimethoxy and diphenyl dimethoxy and diphenyl diethoxy silane, monochlorophenyl diethoxy silane; alkyl alkoxy silanes, as ethyl triethoxy silane, ethyl triisopropoxy silane.

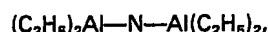
In the catalysts according to the invention the silicon compound is present in combined form in the 10 solid product of the reaction between the various components forming the catalyst in a molar ratio between the silicon compound and the halogenated Ti compound higher than 0.05 and in general comprised between 0.1 and 5.

Other suitable compounds b) are 2,2,6,6-tetramethylpiperidine, 2,2,5,5-tetramethylpyrrolidine, 2,2,6,6-tetramethylpiperidine-Al-diethyl, Al-dichloro-monophenoxy.

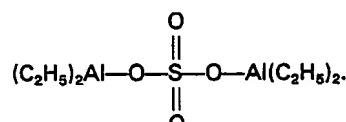
15 The Al-alkyl compounds of component a) include the Al-trialkyls, such as for instance AlEt₃, Al(i-Bu)₃, Al(i-C₃H₇)₃, AlEt₂H, and compounds containing two or more Al atoms linked to each other through hetero-atoms, such as:



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As indicated, Al-alkyl compounds in which Al atoms are linked through groups like SO₄ or SO₃ are also suitable.

The Al-alkyl compounds can be employed in admixture with Al-alkyl halides, as AlEt₂Cl.

Component c) is prepared according to various methods. One of these consists in co-grinding the Mg 35 halide and the electron-donor compound until the product, after extraction with Al-triethyl under standard conditions, shows a surface area higher than 20 m²/g, and in reacting subsequently the ground product with the Ti compound.

Preparations of this type are described in British Patent No. 1,559,194.

Another method consists in reacting an adduct Mg halide/alcohol with a Ti compound in the presence 40 of the electron-donor compound. This method is described in BE—A—868,682.

According to another method, described in DE—A—3,022,738, the adduct Mg dihalide/alcohol is reacted in liquid form with the halogenated Ti compound and with the electron-donor compound.

Other methods are described in DE—A—2,924,029, US—A—4,220,554 and EP—A—15243.

Another method consists in co-grinding the Mg dihalide, the halogenated Ti compound and the 45 electron-donor compound until activation of the Mg dihalide, in treating a suspension of the ground product in a halogenated hydrocarbons, such as 1,2-dichloroethane, chlorobenzene, methylene dichloride, hexachloroethane, and in separating the solid from the liquid halogenated hydrocarbon. This method is particularly suitable for preparing catalyst components satisfying the extractability criterion of the present invention when as electron-donor compounds are employed esters of aromatic monocarboxylic acids, 50 such as alkyl esters of benzoic acid.

The treatment is carried out at temperatures comprised between 40°C and the boiling point of the halogenated hydrocarbon for a time ranging in general from 1 to 4 hours.

According to another method, a porous carrier such as SiO₂ or Al₂O₃ having a low content of OH groups (preferably less than 1% by weight) is impregnated with a liquid adduct Mg dihalide/alcohol; then 55 the carrier is treated with an excess of TiCl₄ containing in solution the electron-donor compound according to the procedure described for example in DE—A—No. 3,022,738 or in BE—A—868,682.

In all the above methods the final product contains a Mg dihalide in the active form as defined hereinafter. For "active form of the Mg dihalide" is meant the Mg dihalides showing in the X-ray powder spectrum of component c) a broadening of at least 30% of the most intense diffraction line appearing in the 60 powder spectrum of the corresponding dihalide having a surface area of 1 m²/g, or is meant the Mg dihalides showing a X-ray spectrum in which said most intense diffraction line is replaced by a halo with its intensity peak shifted with respect to the interplanar distance of the most intense line.

Very active forms of Mg dihalides are those showing a X-ray powder spectrum in which the most intense diffraction line appearing in the spectrum of the corresponding halide having a surface area of 1 65 m²/g has a decreased intensity and is broadened to form a halo, or are those in which said most intense line

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is replaced by a halo having its intensity peak shifted with respect to the interplanar distance of the most intense line.

In general, the surface area of the above forms is higher than 30—40 m²/g and in particular is comprised between 100 and 300 m²/g.

5 Preferred Mg dihalides are MgCl₂ and MgBr₂. The water content of the dihalides in general is lower than 1% by weight.

Other known methods for preparing a Mg dihalide in active form or catalyst components containing Ti and supported on a Mg dihalide, in which components the dihalide is present in active form, are based on the following reactions:

- 10 — reaction of a Grignard compound or of a compound MgR₂ (R is hydrocarbyl) or of complexes MgR₂/Al-trialkyls with halogenating agents, such as AlX₃ or compounds AlRmXn (X is halogen, R is hydrocarbyl, m+n=3), SiCl₄ or HSiCl₃;
- 15 — reaction of a Grignard compound with a silanol or a polysiloxane, H₂O or with an alcohol and subsequent reaction with a halogenating agent or with TiCl₄;
- reaction of Mg with an alcohol and with a hydrogen halide, or of Mg with a hydrocarbyl halide and with an alcohol;
- reaction of MgO with Cl₂ or AlCl₃;
- reaction of MgX₂ · nH₂O (X is halogen) with a halogenating agent or with TiCl₄;
- 20 — reaction of Mg mono- or dialcoholates or of Mg carboxylates with a halogenating agent.

Titanium halides and halogen-alcoholates are in particular the Ti tetrahalides, the Ti trihalides and the Ti trihalogen-alcoholates. Preferred compounds are: TiCl₄, TiBr₄, 2,6-dimethylphenoxytrichlorotitanium and trichloro-phenoxytitanium.

25 The Ti trihalides are obtained by known methods, for instance by reduction of TiCl₄ with Al or with a metallorganic compound of Al or with hydrogen.

In the case of the Ti trihalides it can be expedient, to improve the performance of the catalysts, to carry out an oxidation, even partial, of the titanium during or after the preparation of component c). To this purpose halogens and iodine halides can be employed.

30 Preferred catalysts are those in which component c) is obtained from MgCl₂, TiCl₄ or Cl₃TiOC₆H₅ and esters of maleic or malonic acid or from diisoamyl ether or benzophenone, and in which component b) is phenyl- or ethyl-triethoxy-silane or diphenyl-dimethoxy-silane or diphenyl-diethoxy-silane.

Component a) is an Al-trialkyl, such as Al-triethyl or Al-triisobutyl.

The preferred methods for the preparation of component c) are those described in GB—A—1,559,194, BE—A—868,682, DE—A—2,924,029, US—A—4,220,554, EP—A—15243 or DE—A—3,022,738.

Among the preferred methods for preparing component c) there is also the co-grinding of MgCl₂, TiCl₄ and electron-donor and the treatment of the ground product with a halogenated hydrocarbon, as 1,2-dichloroethane.

35 The catalysts according to the invention are employed to polymerize alpha-olefins by known methods, that is by carrying out the polymerization in liquid phase, either in the presence or in the absence of an inert hydrocarbon solvent, or in gas phase or also by combining, for instance, a polymerization step in liquid phase with a step in gas phase.

In general, the temperature is comprised between 40° and 160°C, but preferably between 60° and 90°C, operating either at atmospheric pressure or at higher pressure.

40 As a molecular weight regulator can be employed hydrogen or another regulator of known type.

The catalysts are particularly suitable for the polymerization of propylene, butene-1, styrene and 4-methyl-pentene-1. The catalysts can also be employed for polymerizing, by known methods, mixtures of propylene and ethylene to produce modified polypropylenes having improved impact resistance at low temperatures (the so called propylene/ethylene block copolymers) or to obtain crystalline random 45 copolymers of propylene with minor amounts of ethylene.

The test for the determination of the complexability of compound b) is carried out by using a potentiograph Metrohm mod. E 536 equipped with titration bench E 535, automatic burette E 552, magnetic stirrer E 549 and titration cell EA 880. It is employed a combined electrode EA 281 (Pt//Ag/AgCl/KCl 3M).

50 As titrating agent is employed a 0.5 M hexane solution of Al-triethyl which is added to a 0.5 M benzene solution of the compound under examination. It is operated at room temperature under nitrogen atmosphere. The test of reactivity of the electron-donor compound with MgCl₂ is carried out under the following conditions.

55 Into a flask of 500 cc capacity are introduced, under nitrogen atmosphere, 2 g MgCl₂ (21 m Moles)

60 suspended in 200 cc toluene and 3.5 m Moles of the electron-donor under examination. It is allowed to react at 25°C for 1 hour and the solid is filtered and washed with 200 cc toluene and then with 200 cc n-heptane. The solid is isolated, dried and analyzed.

As MgCl₂ is employed the product obtained from MgCl₂ · 2.5 C₂H₅OH by reaction with Al-triethyl

according to the following procedure: into a 3000 cc flask are introduced 2340 cc of a 0.83 M hexane 65 solution of Al(C₂H₅)₃; while maintaining the temperature below 10°C, 136 g MgCl₂ · 2.5 C₂H₅OH are added

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little by little. After the addition is completed, it is heated at 70°C for 4 hours; then the solid is filtered, washed repeatedly with n-heptane and dried under a vacuum of 0.2—0.5 Torr.

The surface area of the obtained MgCl₂ amounts to 618 m²/g and the pores volume to 0.532 cc/g.

5 Examples 1—16 and Comparative Examples 1—4. Preparation of the solid catalyst component

10 Into a vibrating mill having a total volume of 1 liter and containing 3 Kg steel balls of 16 mm diameter were introduced, under nitrogen atmosphere, 50 g anhydrous MgCl₂, an electron-donor compound in such an amount as to have a molar ratio MgCl₂/monofunctional electron-donor equal to 6 and a molar ratio MgCl₂/bifunctional electron-donor equal to 12, and TiCl₄ in the molar ratio 1/1 with respect to the electron-donor compound. It was ground for 72 hours. 10 g of the co-ground product were treated with 100 cc 1,2-dichloroethane for 2 hours at 80°C; it was filtered at the same temperature and after several washings with n-heptane the solid catalyst component was suspended in heptane.

15 Polymerization

15 Into a stainless steel autoclave of 3000 cc holding capacity, equipped with magnetic anchor stirrer and thermometer, heat stabilized at 60°C, into which propylene was made to flow, was introduced a suspension consisting of 1000 cc anhydrous and deaerated n-heptane, 5 millimoles aluminum triethyl, the desired amount of the silicon compound and the solid catalyst component.

20 Hydrogen was then introduced at a pressure of 0.2 atmospheres and it was heated rapidly at 70°C while simultaneously feeding in propylene up to a total pressure of 7 atmospheres. Said pressure was kept constant over the whole polymerization time by feeding in continuously the monomer. After 4 hours the polymerization was stopped and the polymer was isolated by filtration and dried. The quantity of polymer dissolved in the filtrate was isolated, weighed and summed to the polymer soluble in boiling n-heptane for the calculation of the isotacticity index (I.I.).

25 The results of the polymerization runs are reported in the Table.

25 In the Table are also reported the results of the tests of extractability with Al-triethyl. The tests were carried out under the following standard conditions: into a 5 liter flask are introduced 4 liter anhydrous and deaerated n-heptane containing 20 m Moles Al(C₂H₅)₃. The temperature is raised to 70°C, about 1 g of solid catalyst component is introduced and the whole is allowed to react under stirring for 15 minutes. Thereupon it is cooled rapidly at 0°C and is filtered, thus isolating a solid which is dried under vacuum at 25°C and analyzed.

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TABLE

Example No.	Solid catalyst component			
	Electron donor (ED)		Extraction with Al(C ₂ H ₅) ₃	
	Type	% by weight (1)	% by weight (3)	Surface area (m ² /g)
1	Di-n-butyl maleate	6.2	0	186
2	Di-n-butyl itaconate			
3	Diethyl allylmalonate			
4	Di-n-butyl malonate			
5	Diisobutyl succinate			
6	Di-n-butyl succinate			
7	Benzophenone			
8	Ethyl trichloroacetate	9.2	0.54	186
9	Ethyl benzoate	8.8	0.8	163
10	Diisoamyl ether (2)	1	0	163
11	α-Methyl-α-phenyl-γ-butyrolactone	7.3	0.9	90
12	POCl ₃			
13	Triphenylphosphine			
14	Ethyl acetate	4.2	0	229
15	O O C ₆ H ₅ —C—O—C—OC ₂ H ₅	9.4	0.3	174
16	Diisobutyl o-phenylene diacetate	6.7	0.9	165
1 compar.	2-Ethylhexylterephthalate	9.2	0.26	1
2 compar.	Phenothiazine	7.7	3.6	
3 compar.	Diisobutyl O,O-diphenyldicarboxylate	6.6	2.4	
4 compar.	Isobutyl m-acetoxybenzoate	8.8	4.2	

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TABLE (continued)

5	Example No.	Polymerization			
		Silicon compound	Al/Si molar ratio	Yield g PP/g catalyst component	I.I. (%)
10	1	(C ₆ H ₅) ₂ Si(OCH ₃) ₂	10	8600	95.1
	2	do	10	4600	93.6
	3	do	10	8500	97.3
15	4	do	10	5000	91.2
	5	do	10	4000	90
	6	do	10	3600	91.5
20	7	do	3.3	3600	93.8
	8	(C ₆ H ₅)Si(OC ₂ H ₅) ₃	3.3	5600	92.2
	9	do	10	4500	95.5
25	10	do	5	5200	91
	11	do	5	3600	91.8
	12	do	5	4000	92
30	13	do	5	3600	90.5
	14	do	10	3200	96.6
	15	do	20	5500	91.3
35	16	do	20	3500	90.7
	1 compar.	do	10	2300	88
	2 compar.	do	10	1300	71.8
40	3 compar.	do	10	trace	—
	4 compar.	do	10	550	84.4
					1.2

(1) The percent amount of ED is referred to the solid after washing with 1,2-dichloroethane.

55 (2) The diisoamyl ether content of the ground product, before washing with 1,2-dichloroethane, was 17%

(3) Percent of ED remaining on the solid of the extraction with Al(C₂H₅)₃.

Claims

- 60 1. A solid component to be employed, in combination with Al-alkyl compounds and with electron-donor compounds which results not to be completely complexed with Al-triethyl at the equivalent point of a potentiometric titration under standard conditions but reactive towards anhydrous Mg chloride, to form catalysts for the polymerization of alpha-olefins CH₂=CHR, said component comprising a titanium compound having at least a Ti-halogen bond and an electron-donor compound both supported on an

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anhydrous Mg dihalide, the electron-donor compound being selected from the group consisting of electron-donor compounds containing N, P and/or S atoms, ethers, ketones, lactones and the following classes of esters:

- 5 1) hydrocarbyl esters of linear saturated dicarboxylic acids having from 2 to 5 carbon atoms;
2) esters of unsaturated polycarboxylic acids in which two carboxyl groups are linked to vicinal, double bond forming carbon atoms and in which the hydrocarbyl radical or radicals of the COOR groups are linear saturated or unsaturated radicals or cycloaliphatic radicals with 1—20 carbon atoms or hydrocarbyl esters of unsaturated linear or branched polycarboxylic acids with 1—20 carbon atoms in which the carboxy groups are not linked to vicinal double bond-forming carbon atoms;

10 3) hydrocarbyl esters of aromatic meta- and para-dicarboxylic acids and hydrocarbyl esters of polycarboxylic aromatic acids containing more than two carboxyl groups;

15 4) hydrocarbyl esters of aromatic hydroxy compounds containing the OH groups in métá- or para-position, and esters of aromatic hydroxy acids the OH groups of which are in métá- or para-position with respect to the carboxyl group;

20 5) esters RCOOR' in which the hydrocarbyl groups R and R', which can be the same or different, are linear saturated or unsaturated radicals or cycloaliphatic radicals having from 1 to 20 carbon atoms, or R is an aryl, alkylaryl or cycloalkyl with 5—20 carbon atoms and R' is a hydrocarbyl radical or a heterocyclic ring with 5—7 atoms in the ring;

25 6) hydrocarbyl esters of polycarboxylic acids in which at least one carboxyl group is linked to an aromatic ring and at least one other is linked to a carbon atom of an aliphatic group or to a cycloaliphatic ring or at least two carboxyl groups are linked to an aromatic ring through an alkylene group;

30 7) esters of aromatic polycarboxylic acids containing at least two non-condensed aromatic ring, each of which bear a carboxyl group;

25 8) esters of carbonic acid with glycols; and carbonic acid derivatives of formula RO—CO—OR' wherein R and R' are the same or different acyl group with 1—20 carbon atoms;

30 9) esters of polyols and of monohydroxy-phenols;

35 10) hydrocarbyl esters of acetylenic acids; the electron-donor compound being extractable from the solid for at least 70% by mols with Al-triethyl under standard measurement conditions, and the surface area of the solid subjected to extraction being higher than 20 m²/g.

2. A catalyst component according to claim 1, in which the electron-donor compound is selected from the group consisting of diisoamyl ether, benzophenone, triphenyl phosphite, di-n-butyl malonate, diethyl allylmalonate, di-n-butyl maleate, ethyl trichloroacetate, propyl trichloroacetate, POCl_3 , 1,6-hexandiol di-n-toluante, and the Ti compound is Ti tetrachloride or trichloro-aryloxy-titanium.

35 al-p-toluate, and the II compound is II-tetrahydro-*n*-octane.

3. Catalysts for the polymerization of alpha-olefins, comprising:

 - an Al-alkyl compound, in particular an Al-trialkyl or an Al-alkyl compound containing two or more Al atoms linked to each other through oxygen or nitrogen atoms or through SO_4 or SO_3 groups;
 - an electron-donor compound reactive, under standard conditions, towards MgCl_2 but not completely complexed with Al-triethyl;
 - the catalyst component of the preceding claims 1 and 2.

4. Catalysts according to claim 3, in which component b) is selected from silicon compounds of general formula:

RmSiYnXp

wherein

R is an alkyl, alkenyl, aryl, arylalkyl or cycloalkyl radical with 1-20 carbon atoms; R₁ and R₂ are different from R.

Y is an $-OR'$, $-OCOR'$ or $-NR'_2$ radical in which R' , the same as or different from R , has the same meaning as R ;

50 X is a halogen or hydrogen atom or a —OCOR'' or —NR'₂ group in which R'', the same as or different from R', has the same meaning as R'; m, n, p are numbers comprised:

m from 0 to 3, *n* from 1 to 4 and *p* from 0 to 1; *m+n+p* is equal to 4.

5. Use of the catalysts according to anyone of claims 3 and 4 for the polymerization of alpha-olefins.

55 Patentansprüche

- 60 1. Eine feste Komponente zur Verwendung in Kombination mit Al-alkylierbindungen und mit Elektronen-Donorverbindungen, die mit Al-triethyl bei einem Gleichgewichtspunkt einer potentiometrischen Titration unter Standardbedingungen nicht vollständig komplexiert wird, jedoch gegenüber wasserfreiem Magnesiumchlorid reaktiv ist, um Katalysatoren für die Polymerisation von α -Olefinen $\text{CH}_2=\text{CHR}$ zu bilden, wobei diese Komponente eine Titanverbindung mit wenigstens einer Ti-Halogenbindung und eine Elektronen-Donorverbindung umfaßt, die beide auf einem wasserfreiem Mg-dihalogenid-Träger sind, wobei die Elektronen-Donorverbindung ausgewählt ist aus der Gruppe, bestehend aus Elektronen-Donorverbindungen, enthaltend N-, P- und/oder S-Atome, Ethern, Ketonen, Lactonen und den folgenden Klassen von Estern:

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- (1) Hydrocarbylester linearer, gesättigter Dicarbonsäuren mit 2 bis 5 C-Atomen;
- (2) Ester ungesättigter Polycarbonsäuren, worin zwei Carboxylgruppen an vicinale, Doppelbindungen bildende Kohlenstoffatome gebunden sind und worin der Hydrocarbylrest oder Reste der COOR-Gruppen lineare, gesättigte oder ungesättigte Reste sind oder cycloaliphatische Reste mit 1 bis 20 C-Atomen, oder Hydrocarbylester ungesättigter, linearer oder verzweigter Polycarbonsäuren mit 1 bis 20 Kohlenstoffatomen, worin die Carboxylgruppen nicht an vicinale, Doppelbindungen bildende Kohlenstoffatome gebunden sind;
- (3) Hydrocarbylester aromatischer meta- und para-Dicarbonsäuren und Hydrocarbylester aromatischer Polycarbonsäuren, enthaltend mehr als zwei Carboxylgruppen;
- (4) Hydrocarbylester aromatischer Hydroxyverbindungen, enthaltend die OH-Gruppen in meta- oder para-Stellung, und Ester aromatischer Hydroxsäuren, deren OH-Gruppen in meta- oder para-Stellung in bezug auf die Carboxylgruppe sind;
- (5) Ester RCOOR', wobei die Hydrocarbylgruppen R und R', die gleich oder verschieden sein können, lineare, gesättigte oder ungesättigte Reste oder cycloaliphatische Reste mit 1 bis 20 Kohlenstoffatomen sind, oder R ist ein Aryl, Alkylaryl oder Cycloalkyl mit 5 bis 20 Kohlenstoffatomen und R' ist ein Hydrocarbylrest oder ein heterocyclischer Ring mit 5 bis 7 Atomen im Ring;
- (6) Hydrocarbylester von Polycarbonsäuren, worin wenigstens eine Carboxylgruppe an einen aromatischen Ring gebunden ist und wenigstens eine andere an ein Kohlenstoffatom einer aliphatischen Gruppe oder an einen cycloaliphatischen Ring gebunden ist oder wenigstens zwei Carboxylgruppen sind an einen aromatischen Ring über eine Alkengruppe gebunden;
- (7) Ester aromatischer Polycarbonsäuren, enthaltend wenigstens zwei nicht-kondensierte, aromatische Ringe, wobei jeder davon eine Carboxylgruppe trägt;
- (8) Ester von Kohlensäure mit Glykolen und Kohlensäure-Derivate der Formel RO—CO—OR', worin R und R' die gleichen oder verschiedene Acylgruppen mit 1 bis 20 Kohlenstoffatomen sind;
- (9) Ester von Polyolen und von Monohydroxyphenolen;
- (10) Hydrocarbylester acetylenischer Säuren; wobei die Elektronen-Donorverbindung aus dem Feststoff zu mindestens 70 Mol-% mit Al-triethyl unter Standard-Meßbedingungen extrahierbar ist und der Oberflächenbereich des Feststoffs, der der Extraktion unterworfen wird, höher als 20 m²/g ist.
2. Eine Katalysatorkomponente gemäß Anspruch 1, worin die Elektronen-Donorverbindung ausgewählt ist aus der Gruppe, bestehend aus Diisoamylether, Benzophenon, Triphenylphosphit, Di-n-butylmalonat, Diethylallylmalonat, Di-n-butylmaleat, Ethyltrichloracetat, Propyltrichloracetat, POCl₃, 1,6-Hexandiol-di-p-toluat, und wobei die Ti-Verbindung Titanetrachlorid oder Trichloraryloxytitan ist.
3. Katalysatoren zur Polymerisation von α-Olefinen, umfassend das Produkt der Reaktion von
- (a) einer Al-alkylverbindung, insbesondere eine Al-trialkyl- oder eine Al-alkylverbindung mit zwei oder mehr Aluminiumatomen, die miteinander über Sauerstoff- oder Stickstoffatome oder über SO₄²⁻ oder SO₃-Gruppen verbunden sind;
- (b) einer Elektronen-Donorverbindung, die unter Standardbedingungen gegenüber MgCl₂ reaktiv ist, jedoch mit Al-triethyl nicht vollständig komplexiert wird;
- (c) der Katalysatorkomponente der vorstehenden Ansprüche 1 und 2.
4. Katalysatoren gemäß Anspruch 3, worin die Komponente (b) ausgewählt ist aus Siliziumverbindungen der allgemeinen Formel

RmSiYnXp

- 45 worin:
- R ein Alkyl-, Alkenyl-, Aryl-, Arylalkyl- oder Cycloalkylrest mit 1 bis 20 Kohlenstoffatomen ist;
- Y ein Rest —OR', —OCOR' oder —NR'₂ ist, worin R' gleich oder von R verschieden ist und die gleiche Bedeutung wie R hat;
- X ein Halogen- oder Wasserstoffatom oder eine Gruppe —OCOR'' oder —NR''₂ ist, wobei R'' gleich oder verschieden von R' ist und die gleiche Bedeutung wie R' hat;
- 50 m, n und p Zahlen sind in dem Bereich:
- m von 0 bis 3, n von 1 bis 4 und p von 0 bis 1; m+n+p=4.
- 55 5. Verwendung der Katalysatoren gemäß irgendeinem der Ansprüche 3 und 4 zur Polymerisation von α-Olefinen.

Revendications

- 60 1. Un constituant solide à employer en association avec des composés Al-alkyle et avec des composés donneurs d'électrons qui ne sont pas totalement complexés avec le triéthylaluminium au point d'équivalence du dosage potentiométrique dans les conditions standards mais réagissant avec le chlorure de magnésium anhydre pour former des catalyseurs convenant à la polymérisation des alpha-oléfines CH₂=CHR, ce constituant étant formé d'un composé de titane présentant au moins une liaison Ti-halogène et un composé donneur d'électrons, tous deux supportés sur un dihalogénure de magnésium anhydre, le composé donneur d'électrons étant choisi dans le groupe comprenant les composés donneurs d'électrons

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contenant des atomes de N, de P et/ou de S, les éthers, les cétones, lactones et les classes suivantes d'esters:

- 1) des esters hydrocarbonés d'acides polycarboxyliques linéaires saturés contenant de 2 à 5 atomes de carbone;
- 5 2) des esters d'acides polycarboxyliques insaturés dans lesquels deux groupes carboxyles sont liés à des atomes de carbone formateurs de double liaison vicinaux et dans lesquels le ou les radicaux hydrocarbonés des groupes COOR sont des radicaux linéaires saturés ou insaturés ou des radicaux cycloaliphatiques comprenant de 1 à 20 atomes de carbone, ou des esters hydrocarbonés d'acides polycarboxyliques linéaires ou ramifiés insaturés comprenant de 1 à 20 atomes de carbone, dans lesquels les groupes carboxy ne sont pas liés à des atomes de carbone formateurs de double liaison vicinaux;
- 10 3) des esters hydrocarbonés d'acides méta- et para-dicarboxyliques aromatiques et d'esters hydrocarbonés d'acides polycarboxyliques aromatiques contenant plus de deux groupes carboxyles;
- 15 4) des esters hydrocarbonés de composés hydroxy aromatiques contenant des groupes OH en position métal- ou para-, et des esters d'acides hydroxy aromatiques dont les groupes OH sont en position méta- ou para- par rapport au groupe carboxyle;
- 20 5) des esters RCOOR' dont les groupes hydrocarbonés R et R', qui peuvent être identiques ou différents, sont des radicaux saturés ou insaturés linéaires ou des radicaux cyclo-aliphatiques comprenant 1 à 20 atomes de carbone, ou R est un radical aryle, alkylaryle ou cycloalkyle comprenant de 5 à 20 atomes de carbone et R' est un radical hydrocarboné ou un noyau hétérocyclique comprenant 5 à 7 atomes dans le cycle;
- 25 6) des esters hydrocarbonés d'acides polycarboxyliques dans lesquels d'au moins l'un des groupes carboxyliques est relié à un noyau aromatique et au moins un autre est relié à un atome de carbone d'un groupe aliphatique ou à un noyau cyclo-aliphatique ou au moins deux groupes carboxyles sont liés à un noyau aromatique par un groupe alkylène;
- 30 7) des esters d'acides polycarboxyliques aromatiques contenant au moins deux noyaux aromatiques non condensés, chacun d'entre eux portant un groupe carboxylé;
- 8) des esters d'acide carbonique avec des glycols et des dérivés d'acide carbonique de formule RO—CO—OR' dans lequel R et R' sont des groupes acyles identiques ou différents comprenant 1 à 20 atomes de carbone;
- 35 9) des esters de polyols et de monohydroxy-phénols;
- 10) des esters hydrocarbonés d'acides acétyléniques; le composé donneur d'électrons étant susceptible d'être extrait du solide par au moins 70% en moles à l'aide d'un triéthylaluminium dans les conditions de mesure standards, et l'aire superficielle du solide soumis à l'extraction étant supérieure à 20 m²/g.

2. Un constituant catalytique selon la revendication 1, dans lequel le composé donneur d'électrons est choisi dans le groupe comprenant l'éther diisoamylque, le benzophénone, le phosphite de triphényle, le malonate de di-n-butyle, l'allyl-malonate de diéthyle, le maléate de di-n-butyle, le trichloroacétate d'éthyle, le trichloroacétate de propyle, POCl_3 , le 1,6-hexanediol -i-p-toluate, et le composé de titane consiste en tétrachlorure de titane ou trichloro-aryloxy-titane.

3. Catalyseurs pour la polymérisation d'alpha-oléfines, comprenant le produit de la réaction de:
a) un composé Al-alkyle, de préférence un Al-trialkyle ou un Al-alkyle contenant deux ou plusieurs atomes d'aluminium, liés entre eux par des atomes d'oxygène ou d'azote ou par des groupes SO_4 ou SO_3 ;
45 b) un composé donneur d'électrons réactif, dans les conditions standards, avec MgCl_2 mais n'étant pas complètement complexé par le triéthylaluminium;
c) le constituant catalytique des revendications 1 et 2 précédentes.

4. Catalyseurs selon la revendication 3, dans lesquels le constituant b) est choisi parmi les composés de silicium de formule générale:



dans laquelle:

- R est un radical alkyle, alkényle, aryle, arylalkyle ou cycloalkyle comprenant 1 à 20 atomes de carbone;
y est un radical —OR', —OCOR' ou —NR'₂ dans lequel R', identique ou différent de R, a la même signification que R;
X est un atome d'hydrogène ou halogène ou un groupe —OCOR'' ou —NR''₂ dans lesquels R'', identique ou différent de R', a la même signification que R';
m, n, p sont des nombres compris:
m entre 0 et 3, n entre 1 et 4 et p entre 0 et 1;
60 m+n+p étant égal à 4.
5. Utilisation des catalyseurs selon l'une quelconque des revendications 3 et 4 pour la polymérisation des alphaoléfines.